

Volatile Constituents of *Valeriana hardwickii* Wall. Root Oil from Arunachal Pradesh, Eastern Himalaya

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Abstract: The composition of the essential oil extracted from *Valeriana hardwickii* Wall. roots growing wild in Talle Valley of Arunachal Pradesh, Eastern Himalaya was analyzed by capillary GC and GC/MS. Thirty-one compounds representing 89.6% of the total oil were identified. The oil was found to be rich in sesquiterpenes from which oxygenated sesquiterpenes (25.7%). Methyl linoleate (21.1%) and Valeracetate (11.6%) were the major constituents present in the oil. Whereas, Bornyl acetate (11.2%) and α -Terpinyl acetate (4.7%) were the only oxygenated monoterpenes identified in the investigated sample. Essential oil and its constituents of *V. hardwickii* may be used as the substitute of highly traded Indian Valerian (*V. jatamansi*) and European *V. officinalis*.

Keywords: *Valeriana hardwickii*; GC-MS; volatile oil; Valeracetate; Methyl linoleate.

1. Plant Source

Valeriana hardwickii Wall. (Fam.; Valerianaceae) is a perennial herb with thick creeping rootstock and distributed in Himalayas from Kashmir to Bhutan at an altitude of 1800-3500m and Khasi hills of Northeast India between 1200-1800m [1]. The roots and rhizomes of this genus are bitter, carminative, diuretic, expectorant, nervine and stimulant by nature [2].

The fresh roots of *V. hardwickii* were collected in October 2009 from Talle valley (N27° 32' 474" E093° 55' 677") of Arunachal Pradesh, Eastern Himalayan region at an altitude of 2420m.

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Plant species was identified and a voucher specimen (MAO, 19294) was deposited in 'ARUN' Herbarium, Botanical Survey of India, Arunachal Pradesh Regional Centre, Itanagar.

2. Previous Studies

Volatile oil constituents of *V. hardwickii* var. *arnottiana* were reported from Uttaranchal, Western Himalayan region [3]. Epoxysesquithujene, a new sesquiterpene epoxide was characterized in the essential oil of *V. hardwickii* var. *hardwickii* [4].

Several species of this genus has long been used by the Ayurvedic, Unani and modern pharmaceutical industries globally for their high medicinal values curing epilepsy, insanity, nervous disorders, obesity, etc [5, 6]. But, there is no report on the medicinal use of *V. hardwickii*.

This is the first chemical report on terpenoid compositions of *V. hardwickii* from the Talle Valley of Arunachal Pradesh, Eastern Himalaya.

3. Present Study

Freshly harvested plant materials (100 g) were subjected to hydrodistillation in a Clevenger type apparatus for 3 h. The oil was dried over anhydrous sodium sulphate and stored in a refrigerator at 4 °C prior to analysis.

The GC–MS analysis of the oil was performed on a Perkin Elmer Auto XL GC interfaced with a Turbomass Quadrupole mass spectrometer fitted with an Equity-5 fused silica capillary column (60 m x 0.32 mm i.d., film thickness 0.25 µm; Supelco Bellefonte, PA, USA). The oven temperature program was the same as described in capillary GC; injector, transfer line and source temperatures were 250 °C; injection size 0.03 µL neat; split ratio 1:30; carrier gas He at 10 psi constant pressure; ionization energy 70 eV; mass scan range m/z 40-450 amu.

The GC analyses of the oil samples were performed on a capillary Perkin-Elmer Auto XL GC equipped with an Equity-5 column (60 m x 0.32 mm; film thickness 0.25 µm; Supelco Bellefonte, PA, USA). The column oven temperature ranged from 70–250 °C, programmed at 3 °C/min, with initial and final hold time of 2 min. Hydrogen was the carrier gas at 10 psi constant pressure 1.0 mL/min. The injector and detector (FID) temperatures were 250°C and 280°C respectively. The injection volume was 0.03 µL neat and the split ratio was 1:30.

The identification of the chemical constituents was assigned by based on their retention indices (relative to *n*-alkane C₉-C₂₂), MS Library search (NIST/EPA/NIH version 2.1 and Wiley registry of mass spectral data 7th edition.) and by comparing the mass spectra with MS literature data [7, 8]. The relative amount of the individual components was calculated from the peak area without applying an FID response factor correction.

The essential oil compositions presented in Table 1. revealed that the investigated *V. hardwickii* roots yielded 0.3% (v/w) volatile oil from which thirty-one compounds were characterized and identified by GC-MS, accounting for 89.6% of the total oil.

The volatile oil was mainly composed of oxygenated sesquiterpenes (25.7%) including Valeracetate (11.6%), Cuparene (7.1%) and β-Acoradienol (3.5%) as the major components. Whereas, α-Gurjunene (3.1%) and α- Guaiene (2.4%) were the dominant compounds among sesquiterpene hydrocarbons. Excluding terpenes, a methyl ester of lenoleic acid typified as Methyl linoleate (21.1%) was found to be the active marker in our sample. Also this fatty acid was reported in the earlier studies from *V. hardwickii* var. *arnottiana* oil [3]. Bornyl acetate (11.2%) and α-Terpinyl acetate (4.7%) were the only oxygenated monoterpenes identified in the investigated sample.

The sesquiterpene ester Valeracetate from the root oil of European *V. officinalis* has been used for the sedative and antispasmodic purposes. Also in the present report Valeracetate was found as a major constituent in the root oil of *V. hardwickii* for which it may be used as a substitute of *V. officinalis*. Maaliol and Patchouli alcohol were reported as the major components of Indian Valerian

(*V. jatamansi*) isolated from Northwestern Himalayas [9]. However, in our investigation Maaliol content was 0.9% and Patchouli alcohol was not detected in the sample.

Table 1. Volatile oil constituents of *V. hardwickii* from Talle Valley of Arunachal Pradesh, Eastern Himalaya

Compounds	Peak area (%)	KI ^a	KI ^b
α - Pinene	4.1	935	938
Camphene	0.3	946	950
γ - Terpinene	t	1061	1060
Bornyl acetate	11.2	1288	1285
α - Terpinyl acetate	4.7	1347	1345
α - Longipinene	1.6	1356	1360
β - Elemene	t	1388	1391
α - Cedrene	1.7	1402	1396
α -Gurjunene	3.1	1419	1410
β -Caryophyllene	0.1	1423	1419
α -trans-Bergamotene	0.9	1434	1436
α - Guaiene	2.4	1436	1439
Seychellene	0.1	1442	1447
α -Humulene	0.7	1452	1454
<i>allo</i> -Aromadendrene	2.1	1458	1461
<i>ar</i> -Curcumene	1.1	1481	1483
β - selinene	t	1486	1485
β -Guaiene	0.1	1492	1495
γ -Cadinene	0.9	1498	1502
Cuparene	7.1	1504	1509
Kessane	2.8	1512	1518
γ -Bisabolene	0.6	1537	1539
Maaliol	0.9	1568	1565
Viridiflorol	1.5	1594	1592
Vulgarone B	0.9	1638	1641
Bulnesol	0.4	1663	1669
β -Acoradienol	3.5	1739	1736
Drimenol	1.8	1745	1750
α -Kessyl acetate	2.3	1774	1781
Valeracetate	11.6	1921	1925
Methyl linoleate	21.1	2076	2082
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Monoterpene hydrocarbons	4.4		
Oxygenated monoterpenes	15.9		
Sesquiterpene hydrocarbons	22.5		
Oxygenated sesquiterpenoids	25.7		
Others	21.1		
Total identified	89.6		

^aKovats index experimental (Equity-5 column; relative to *n*-alkane)

^bKovats index literature

t: trace components (<0.1%)

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